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2018

Enroth , J , Kangasluoma , J , Korhonen , F , Hering , S , Picard , D , Lewis , G , Attoui , M & Petäjä , T 2018 , ' On the time response determination of condensation particle counters ' , Aerosol Science and Technology , vol. 52 , no. 7 , pp. 778-787 . <https://doi.org/10.1080/02786826.2018.1460458>

<http://hdl.handle.net/10138/308191>

<https://doi.org/10.1080/02786826.2018.1460458>

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On the time response determination of condensation particle counters

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Abstract

Condensation particle counter (CPC) technology has continued to evolve, with the introduction of several new instruments over the last several years. An important aspect in the characterization of these instruments is the measurement of their time response. Yet there is no standardly accepted approach for this measurement. Here we evaluate different classically used methods for determining CPC time response, and present the potential pitfalls associated with these approaches. Further, we introduce a new simple definition for the term response time, ϵ , which is based on the first-order systems response, while providing a practical definition by corresponding to ~ 95 % change in concentration. We also present results for various commonly used CPCs, and for the Airmodus A11 nano Condensation Nucleus Counter (nCNC) system, the TSI 3777+3772 Nano Enhancer system, and Aerosol Dynamics Inc.'s (ADI) new versatile water condensation particle counter.

1 Introduction

Condensation particle counters (CPCs) with a fast time response are required in numerous instances where rapid changes in the particle concentration are of interest. Applications include measurements under transient conditions, monitoring done aboard mobile platforms, studies relying on eddy covariance, and fast-scanning mobility particle sizing (e.g. Buzorius et al. 1998; Drewnick et al. 2012; Held and Klemm 2006; Kolb et al. 2004; Pirjola et al. 2004; Weijers et al. 2004). Often a response time of less than one second is needed. Yet, most CPCs are relatively slow instruments, responding to concentration changes on the time scale of some seconds (Quant et al. 1992). On the other hand, some instruments, like the custom mixing type CPC designed by Wang et al. (2002) and commercialized by Brechtel Manufacturing Inc. was specifically designed to provide a fast time response. Other fast commercial instruments include some of the water based condensation particle counters by TSI Inc. and Aerosol Dynamic Inc. as well as some of the sheathed butanol based CPC's. Tröstl et al. (2015) showed that some of these CPCs are suitably fast for allowing even sub-10 second size distribution scans when combined with a differential mobility analyzer (DMA).

Although several types of CPCs have been specifically designed for their speed, there is no generally accepted method for determining their time response. Indeed, there is not even widely adopted terminology. Different studies have used different approaches to create the rapid changes in particle concentration required to determine the CPC time response. Moreover, the methodology description in

most published studies lacks key parameters such as the flows, tubing diameters and the concentrations that were used.

The poor determination of the instruments time response is not only a problem for the manufacturers, but it can potentially distort measurement data as the users might not know the limitations of their instruments. In cases where high instrument sampling rates are used, for instance in flux measurement, incorrect response time can mean biased sampling, i.e. underestimation of the magnitude of the actual concentration changes due to the instruments slowness, which in theory would reduce the observed flux. Correspondingly in other rapidly changing conditions, such as mobile measurements, a slow instrument will act as a low pass filter if the sampling is done faster than permitted by the instruments response time. For accurate particle sizing measurements, especially for the Scanning Mobility Particle Sizer (SMPS), precise knowledge of the CPCs response time is vital in order to match the observed concentration and applied voltage. Although for non-continuous applications, such as the SMPS, also the initial time delay is of great importance.

A CPC's time response consists of two parts. The first, t_{delay} , is the minimum lag time associated with particles passing through a CPC, i.e. the time taken for the fastest particles to travel from the inlet to the detector. The second, t_{mixing} , describes the difference in the travel times between the fast and slow-moving particles within the instrument and is commonly known as the mixing time. In practice, t_{mixing} describes the instruments response to a changing concentration. Therefore, our focus here is on the mixing time, and it also will be the portion of the time response that we will refer to when talking about response times.

The motivation for the work emerged while trying to determine the time response of a new mixing type CPC, designed by Michel Attoui at the University Paris Est Creteil, and built at the University of Helsinki. Our initial time response measurements showed inconsistencies in many of the previously reported approaches (Buzorius 2001; Quant et al. 1992; Wang et al. 2002). This led to the discovery of potential pitfalls in determining the time response of a fast CPC - pitfalls which can lead to both over- and underestimation of the studied instruments response time. Here we address these issues and compare the different methodologies that have been used in the literature. Besides introducing the potential problems associated with measuring CPC time response, the additional aim of this paper is to introduce suitable methods for measuring response times with high reproducibility. We also aim to promote more rigorous reporting of important key parameter such as the flows and diameter of the tubing used, or the Reynolds numbers in the tubing, and very importantly the actual particle number concentration used to measure the response time. We also present response time data from a CPC-workshop and intercomparison organized at the University of Helsinki in the summer of 2016 (Kangasluoma et al. 2017).

2 Methodology

Response time describes the characteristic response of a CPC when it faces an instantaneous change in particle number concentration. Even if the concentration change would be truly instantaneous, the response would not be an ideal step change, rather it would be smeared out as the particles travel at various speed inside the CPC due to the laminar flow velocity profile. The time response is also affected to a lesser extent by diffusion within the instrument. The amount of smearing is dependent on the geometry and the flows used by each instrument, but the general resulting pattern is close to a first order response, and thus is well described with the exponential function:

$$N(t) = N_1 + (N_0 - N_1) * \exp\left(-\frac{t-t_0}{\tau}\right) \quad (1)$$

Where τ is the time constant, N_1 is the final concentration, N_0 the initial concentration, t is time and t_0 is the time of concentration change onset. τ , also referred to as mixing time describes the smearing effect and is likely the most common piece of terminology used in the literature (e.g. Held and Klemm 2006; Hering et al. 2017; Hering et al. 2005; Wang et al. 2002; Wehner et al. 2011). The responses theoretical derivation can be found in Doebelin (1990). The fit provides a suitable approximation of the CPC concentration response to be useful here, even though the fit does not perfectly describe all instruments or methods, e.g. the DMA method or the TSI 3777+3772 Nano enhancer system. However, for most methods and instrument this provided a good fit, and therefore we continue to use this form of the formulation, which has also been used in previous work for describing the change in concentration with respect to time (Hering et al. 2005; Wehner et al. 2011). We also base the description of the instruments response on the mixing time, but apply it so that response time is defined as:

$$\varepsilon = 3 * \tau \quad (2)$$

This definition makes the term response time more practical as $3 * \tau$ corresponds to a 95 % concentration change (more accurately 95.021...%). We favor this approach, as this definition yields more information on the instruments response than reporting e.g. the 10, 50 and 90 % response times (as these can all be calculated using the τ), while maintaining the clarity and simplicity suitable even for the non-expert instrument user, which minimizes the potential for misunderstanding the instrument behavior. Table S1 provides a comparison of observed 10, 50, 90 and 95 % response times, and corresponding response times calculated based on the fit given in Eq. 1 for select CPCs.

The mixing time based definition is further useful as it allows the response time to be determined from any part of the concentration change curve, due to the exponential nature of the definition, so long as the final concentration is known, and the instrument response is well described with Eq. 1. This means that one does not necessarily have to utilize the whole range of concentration changes. This is useful, as it can be difficult to determine the exact timing of the concentration change start or end.

It should be noted that smearing, however, occurs also in the piping leading to the instrument, making it of utmost importance to ensure that the any flows leading up to the instrument are turbulent. Turbulent flow, unlike laminar flow, has a plug flow velocity profile, i.e. the air parcel in the tube moves at a uniform speed so smearing of the aerosol signal should be minimal. If the flow is not turbulent, the observed response time will not describe only the instrument, but the combined effect of the sampling set-up and the instrument, giving thus too slow response times.

Based upon this understanding of the phenomena, there is no immediately obvious reason why the response of a CPC should differ when measuring the response from a concentration increase or a concentration decrease. This, however, is what has been observed by some previous studies (Quant et al. 1992; Shi et al. 2005). Curiously, other studies have not found this effect, for instance Hering et al. (2005). One potential explanation for the phenomena is the presence of unswept volumes in the aerosol flow path. These would have a minimal effect for an increasing aerosol concentration, while a much larger effect in the opposite case. This is also what is observed; when the bias is present it acts to make

the concentration decay time longer, and therefore more focus is given to the decay process here, as it seems to be the limiting response.

Various methods used in the literature for producing a sharp concentration step change were studied here. Most common methods in the literature involve either the use valves (Heim et al. 2004; Held and Klemm 2006; Hering et al. 2005; Quant et al. 1992), spark generators (Hering et al. 2017; Shah and Cocker 2005; Wang et al. 2002) or DMAs (Buzorius 2001). Also ambient sampling (Wehner et al. 2011) and manual filter placement (Hering et al. 2017; Stolzenburg and McMurry 1991), and electrostatic precipitators (Oberreit et al. 2014) have been used, but these were not included here.

All results presented here are measured at concentration below 5000 cm^{-3} and measurement setups had turbulent ($\text{Re} > 3000$) flows in sampling lines unless otherwise stated. All measurements were repeated numerous times, with minimum of 19 repetitions for each method-instrument combination. The data from the various CPCs was gathered by reading the pulse output of the CPC's, rather than the serial output, due to the ability to sample faster. The sampling was performed either at 100 or 50 Hz for all instruments and logged with a LabJack DAQ card.

2.1 DMA

The first method for the particle concentration control was a rapid voltage control of a DMA. By changing the voltage in the DMA suddenly from a preset value to zero, or vice versa, one should be able to produce a step change in the particle concentration. This method has been successfully used by Buzorius (2001) for studying a modified TSI 3010 with varied inlet flow rates. DMA's have also been used by Shi et al. (2005), where the authors used tandem-DMA system where the first DMA was used to select monodisperse particles, and the second for producing the step change in concentration. Setup used here is described in Fig. 1.

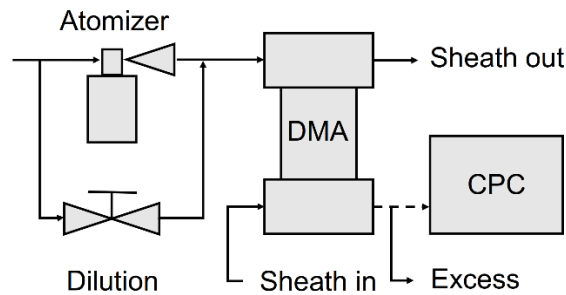


Figure 1. The DMA setup. A Vienna type DMA with 4 liters per minute (lpm) aerosol flow rate and 20 lpm sheath flow rate. A 4 mm inner diameter (ID) Swagelock T-cross was connected to the DMA outlet with the one path attached to the CPC inlet, and the other was an excess outlet. Length of the dashed line was minimized.

2.2 SPARK

The second method tested was the spark generator, which has been shown to be a reliable method to produce aerosol particles (Schwyn et al. 1988). The spark generator consists of two electrodes that are

brought close to each other. Once high enough voltage to exceed the breakdown voltage of air is reached, a spark will form between the electrodes. The formation of the spark evaporates some of the electrode material, which then cools to form a very transient high concentration particle pulse of small particles. The exact size of the particles is dependent on the electrode material, the voltage and the flow used. This method has been used by Wang et al. (2002) as well as Shah and Cocker (2005). Here we used a homemade spark generator built into a stainless steel four-way connector piece with a 16 mm ID (Schwyn et al. 1988). The setup used here is presented in Figure 2.

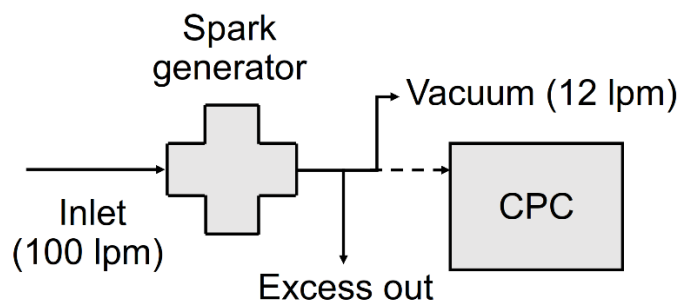


Figure 2. The spark generator setup. 100 lpm particle free air was passed through the generator in a 10 mm ID piping, which simultaneously diluted the spark generated aerosol to suitable concentration levels. From the main flow we sampled 14 lpm to a 4 mm ID side branch, ending in a T-cross connected to a vacuum line for the additional flow and the inlet of the instrument being tested. Length of the dashed line was minimized.

2.3 VALVE

The final tested method was a variation of the valve method as used by for instance by Quant et al. (1992) and Hering et al. (2005). We experimented with different implementations of the method; setups included ones with generation of aerosol and ambient sampling, as well as the use of differing flow rates. The first set up was operated with an atomizer, producing 4 lpm aerosol (ammonium sulfate particles) flow, which was mixed with a 40 lpm carrier flow. Setup is presented in Fig. 3.

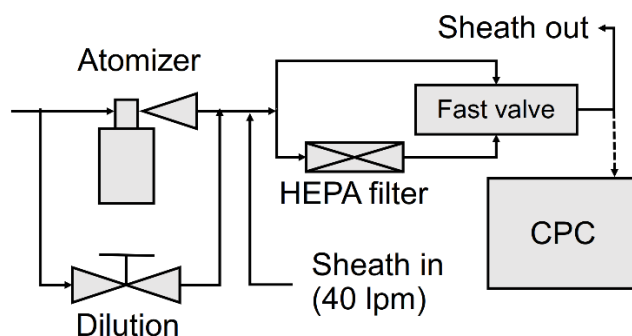


Figure 3. Initial valve setup. Atomizer generated aerosol along with 40 lpm carrier flow was led to the fast valve via a filtered and an unfiltered path. The challenged CPC's were connected directly to a T-cross connected the exit of the valve, and an excess flow outlet path. In total the piping between the T-cross and CPC inlet (dashed line) was < 3 cm and the inner diameter of the piping used was 4 mm.

Second setup consisted only of the valve placed at the mouth of the CPC, removing thus virtually all piping between the CPC and the valve (total length being < 1 cm), with a filter attached to one of the paths, while the other one being open to the ambient (Fig. 4a). The third valve based set up had again the atomizer as the aerosol source, but here the focus was to keep the aerosol flow as low pressure as possible, so here the valve was again at the mouth of the inlet, one path being filtered ambient, and the other coming from an atomizer, which was held near ambient pressure (Fig. 4b).

Figure 4.

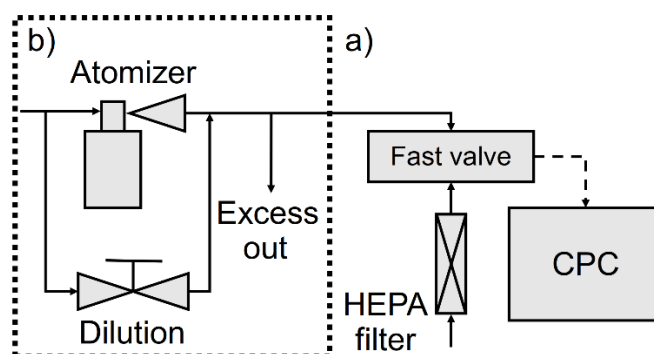


Figure 4. a) The simple valve setup, consisting of only a filter and sampling from the ambient. b) The low-pressure atomizer setup included an atomizer as the aerosol source held at ambient pressure.

The type, and speed of the valve used can also influence the measurement results. Typical valves can have switching times of some tens of ms, which is on the order of the response of the faster CPCs around. Therefore, care should be taken in choosing a suitably fast acting valve. Here we chose to use a Festo MH2 valve, with a reported switching time of 2 ms (Festo 2016).

2.4 TEST CPCs

Measurements were performed on nine different CPC models. Five butanol based laminar flow instruments: TSI 3776 which is a sheathed, the TSI 3010, TSI 3772 and Airmodus A20 which are all unsheathed, and the B3010 which is similar in geometry to the TSI 3010 but operated at higher temperature differential (Kangasluoma et al. 2017). Two other laminar flow instruments examined are the TSI 3777+3772, a sheathed diethylene glycol instrument coupled to a TSI 3772, and the ADI vWCPC (Hering et al. 2017), an unsheathed, <2-nm water-based instrument. The nCNC A11 by Airmodus, which is a combination of a mixing type particle size magnifier (A10) and the laminar flow A20 CPC. The final CPC, UHEL FCPC, was a mixing type butanol-based instrument. A summary of the relevant CPC parameters is given in Table S2.

3 Results

3.1 DMA

The speed at which a change in particle number concentration can be achieved with a DMA is dependent on the type of DMA, the sheath and sample flows used, and the power source, assuming the influence of the sampling lines can be ignored. We found that the set up available here was not suited for producing a steep enough step change, in order to characterize the faster CPCs, despite minimizing tube length, and using highest possible flows for this type of DMA. Possible sources of error included the time response of the power source, width of the transmission function of the DMA or other DMAs geometry-based limitations. For the measurement made with the TSI 3776 (high flow, 1.5 lpm), the observed response times with this method were found to be 0.5 s and 0.33 s for the concentration decay and increase, respectively. Both values are longer than the response time calculated for the 3776 based on the values provided by the manufacturer of ~ 0.21 s (Fig. 5).

However, the DMA method would likely be suitable for response time determination, provided that high flow DMAs with sub 1 ms response times (Fernandez de la Mora 2011), along with fast power sources, were used.

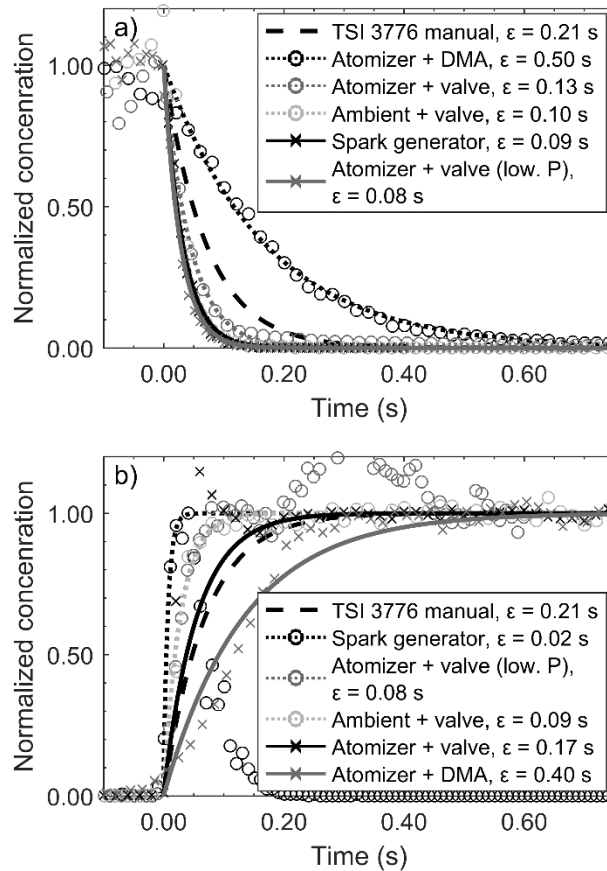


Figure 5. The influence of the different methods used in literature for determining the response time of a TSI 3776. Note that the response time of concentration increase as determined by the spark method is strongly underestimated and is provided to exemplify the issues with this method. See Figure S1. for a version plotted on logarithmic axis.

3.2 SPARK

(omitted words)Spark generator produces a short high concentration pulse of particles, each time a spark is given off. The use of spark generator requires a high carrier flow for both dilution and ensuring turbulent flow in the sampling lines. However, rapid dilution means faster cooling of the metal vapors, resulting in a smaller mean particle diameter and a corresponding increase in the number concentration, which can exceed $1\text{e}7\text{ cm}^{-3}$ (Meuller et al. 2012). This creates a need for even further dilution, which can either be implemented by filtering a portion of the flow or by increasing the carrier flow further. The increase of carrier flow was chosen here to avoid potential smearing problems caused by the filter. By increasing the flow rate in the spark chamber up to 100 lpm, we were able (omitted words)to bring the particle concentration down to $< 5000\text{ cm}^{-3}$. The large carrier flow also ensures (omitted words) turbulent flow, provided that typical tubing sizes are used (ID $\sim 10\text{ mm}$ and smaller).

If dilution is insufficient or not used, the spark method is likely to yield concentrations high enough to cause coincidence in the CPC optics. The concentration at which coincidence begins to be significant differs between different instruments, but once present it will distort the observed response time of the instrument by making it shorter for the concentration increase and longer for the concentration decay (see Figure 6). This is also what was reported by Hering et al. (2017) where they observed higher concentrations yielding longer response times. Coincidence will cause the instrument to miss a portion of the particles, and hence create a false plateauing in the observed concentration while the actual particle concentration can keep increasing. See for instance the appendix in Hering et al. (2005). The concentration problem of course applies for all other methods also, not only the spark; however, most other particle generation methods allow for finer particle concentration control. To ensure that this problem is avoided, the absolute and not only normalized, concentration should also always be reported while publishing data on response times.

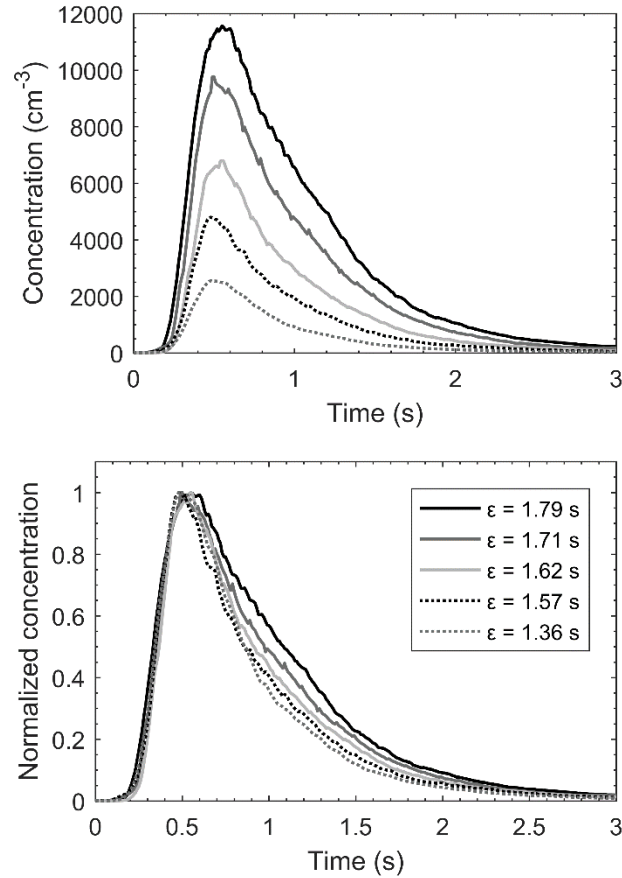


Figure 6. Averaged response times for different concentrations, showing the coincidence induced response time dependency on concentration. The data is from the B3010 at high flow settings (1.6 lpm), which optics have 7.4 % coincidence already at concentration 10^4 cm⁻³. The standard deviation for all levels was less than 0.01 s. Although not noticeable here, the coincidence induced distortion should also appear as a shorter response time for the concentration increase.

Besides the high concentration, the extremely transient nature of the particle pulse can be problematic. The (omitted words) particle pulse is very short lived, meaning that for most instruments the concentration will start decreasing, before instruments response has been saturated, i.e. the mixing time of the CPC is longer than the duration of the spark. This means, that there is no stable maximum concentration to be observed, nor can the value of the true maximum be known. (omitted words) Thus any response time determined from a spark generator created concentration increase will be missing the slowest part of the change, and this will bias the response time to be faster than it is in real life, as shown in Figure 5. Therefore, concentration increase response times measured with the spark should be suspect, until it has explicitly shown that this has not distorted the results, by for instance showing a symmetric decay function. Here, we disregard the spark concentration increase data due to these reasons.

Another caveat in the use of the spark generators (omitted words) is the impact of particle size. Depending on the operational parameters of the generator, such as the spark energy, flow through spark chamber, rate of sparking etc., the resulting particle size distribution can change dramatically (Evans et al. 2003; Schwyn et al. 1988; Tabrizi et al. 2008). Reducing the concentration to suitable levels via dilution can reduce the modal particle diameter, even down to < 10 nm. This is problematic for CPCs

having a cutoff limit in the same region as only the portion of the particles experiencing the highest supersaturation will activate. As the highest supersaturation coincides with the fastest moving portion of the flow, the response of the instrument will be biased towards unrealistically fast response times. This was what was observed in the case of the TSI 3010 here, as explained further in section 3.4. This reasoning is further supported by the response time measured for the boosted 3010, which was found to have very similar response time to that measured for the normal 3010 with a valve, and where the size distribution was not a factor. One should therefore ensure that the size of the particles used is well above the detection limit of the instrument being tested.

Despite these limitations, the spark generator can still be useful in determining instrument response times. (omitted words) The concentration decay, provided that coincidence is not present, and suitable particle size distribution is used, should (omitted words) be a reliable method for response time determination. Although the maximum concentration cannot be known from a spark generator, it is not needed when one uses the first order response assumption. Fitting Eq. 1 to any point of the decay curve should produce the same result, producing the response time of the instrument. It should be noted however, that this methodology is not applicable if coincidence is present, as this will distort the fit to an unknown extent (Fig. 6). Here we found a good agreement between the spark method and the alternative valve method as show in Figure 5.

3.3 VALVE

The valve method has been widely used in the field for instrument response time measurements for instance Quant et al. (1992), Hering et al. (2005), Heim et al. (2004) and Held and Klemm (2006). This method provides a sharp step change that can be maintained for extended time periods. This allows for the response time to be determined for both concentration increase and decay. The simplest implementation of this is to place a three-way valve right at the inlet of the challenged CPC, and have one path sampling from ambient, and the other through a filter. In order to have better control of the parameter space, i.e. the type and size of aerosol, and concentration, one can attach also an atomizer (and DMA, if size control is wanted) before the valve.

The use of a valve was however associated with pressure related issues in some CPCs. The issue is a minor one in the cases where the sample is ambient air, as the pressure change between the filter and the ambient is smaller, and made worse by the use of atomizer, or any further over pressure on the system. The issues are observed in both the faster sheathed instruments such as the TSI 3788 and 3776, and in some of the laminar flow instruments, like the Airmodus A20.

As the valve switches there is discontinuity in the sample flow. When closing the aerosol flow path, a momentary negative concentration spike was observed. This could be due to the flow stopping in the instrument or the saturation ratio being lowered so that particles did not activate. The opposite was found for opening the aerosol path i.e. it was associated with a positive spike in concentration. (omitted words and rewording of chapter)

The initial valve method included the use of an atomizer as the aerosol source, and a large carrier flow to reach turbulent conditions for the sampling lines. This provided initially good results, agreeing with the literature values for the TSI 3010 for instance ($\epsilon = 2.3$ s vs $\epsilon_{\text{Quant}} = 2.7$ s; Quant et al. (1992)). This solution allowed fine control of most of the parameters involved (composition, stable concentration), and it was easy to gather large amounts of data with high reproducibility using this set-up. However, the high carrier flow caused the system to be operated above ambient pressure, which made

the pressure related spikes considerably worse and constantly present, especially with sheathed instruments. Also, the agreement with the response times measured by the spark method was not perfect, and there was a clear bias which grew worse with the faster instrumentation. (omitted words and rewording of chapter)

In order to get rid of the pressure related issues, a simpler valve implementation was tested, where the sampling was done either directly from the ambient or through a filter. This allowed for no control over the sampled aerosol and at ambient concentrations ($\sim 1000 \text{ \# cm}^{-3}$), for instance the 3776 recorded only ~ 8 counts per sample, when sampling at 100 Hz. Such low counts make the accurate determination of the response time difficult and increase the relative influence of random variation. This however was found to be a suitable method when the resulting concentration is high enough to provide good counting statistics. (omitted words and rewording of chapter)

To improve the counting statistics, an atomizer was added as an aerosol source, while trying to maintain a pressure at near ambient levels in the aerosol line. The low-pressure valve method was found to agree well with the spark generator method. Although the particles were not size selected, for neither the valve nor the spark measurements, this is not believed to affect the time at which particles reach the CPC optics, based on comparison measurements between mono- and polydisperse particle sizes, shown in Figure 7. (omitted words and rewording of chapter)

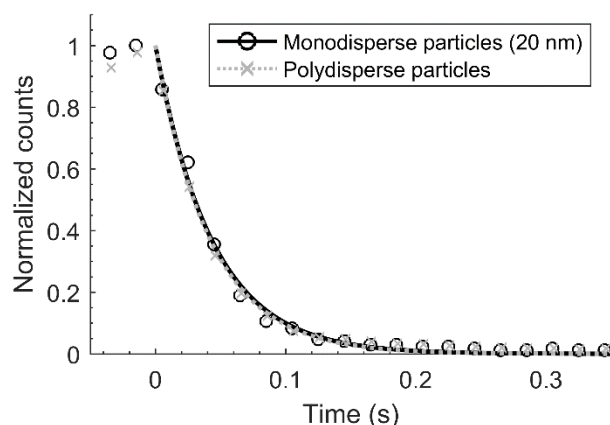


Figure 7. The response time of TSI 3776 measured using the valve method, for non-size selected particles (polydisperse) or 20 nm particles (monodisperse). It should be noted that the measurement method used is too slow for the CPC in question, but the results do show that the size of the aerosol in this range has only a negligible effect on the determined response time. See Figure S2. for a version plotted on logarithmic axis.

4 CPC workshop

During the summer of 2016, a CPC workshop was held at the University of Helsinki (Kangasluoma et al, 2017). During the workshop, the response times of various CPCs were studied. These included the versatile water CPC (v-WCPC) by Aerosol Dynamics Inc. (Hering et al. 2017), 3777 Nano Enhancer, 3776 and 3788 by TSI, a custom boosted CPC based on the TSI 3010 (B3010) from Clermont Ferrand University and an in-house built mixing type CPC from University of Helsinki (FCPC). The results for spark based measurements are presented in Figure 8, while the response times

for both the spark and fast valve based measurements are summarized in Table 1. Not all instruments were available for both valve and spark measurements, hence some of the values in the table are missing.

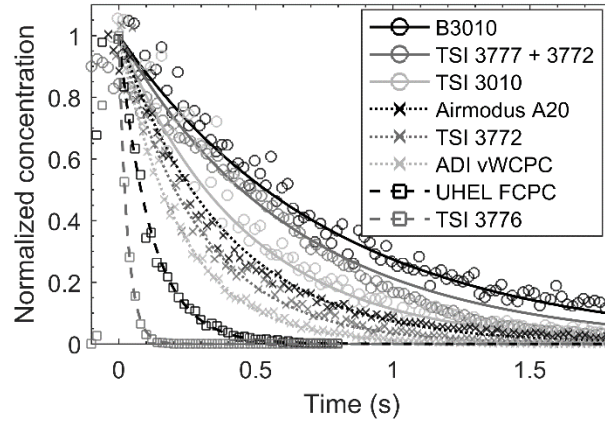


Figure 8. The response time various CPCs and the instruments presents at the CPC workshop, as determined by the spark method. Due to the methods limitations, no concentration increase times could be measured. See Figure S3. for a version plotted on logarithmic axis.

The geometry of the B3010 instrument is based on the TSI 3010, and the response time should also be similar. Utilizing the spark method, we found the response time for the B3010 to be 2.32 s, which is closer to those reported by Buzorius (2001) 2.49 s and Quant et al. (1992) 2.7 s, than that reported by Wang et al. (2002) 4.05 s. For the TSI 3010 we found $\varepsilon_{\text{spark}}$ to be 1.37 s, while $\varepsilon_{\text{valve}}$ was found to be 2.26 s. The discrepancy is due to the partial activation of the particles in the regular 3010. The particle size produced by the spark generator coincides with the cutoff region of the TSI 3010. The result was that the slowest moving particles nearer the instrument walls did not activate, while the faster moving particles near the centerline, and highest supersaturation did, biasing the instruments response to appear considerably faster than it actually is. The same phenomena can explain the observed difference in the response time of the 3772 between the valve and spark methods.

*Table 1. Summary of measured response times in seconds. The range of values given for the Airmodus A11 is due to the different flow settings available for A10. *The times reported with the spark method are distorted for the TSI 3010 and 3772, see section 3.4*

| | Spark, decay | Valve, increase | Valve, decay |
|-------------------|-----------------|--------------------|-----------------|
| ADI wCPC | 0.68 | - | - |
| Airmodus A11 nCNC | - | 1.62–1.74 | 1.48–1.72 |
| Airmodus A20 | 1.15 | 1.13 | 1.08 |
| B3010 | 2.32 | - | - |
| B3010 (1.6 lpm) | 0.91 | - | - |
| TSI 3010 | 1.37* | 2.07 | 2.26 |
| TSI 3772 | 0.89* | 1.32 | 1.3 |
| TSI 3776 | 0.09 | 0.09 | 0.1 |
| TSI 3777+3772 | 1.94 | - | - |
| TSI 3788 | - | 0.12 | 0.12 |
| Uni. Hel. FCPC | 0.35 | - | - |

The 3777+3772 combination and the B3010 were found to have the slowest response times, although this is to be expected, given that the focus of these instruments is in probing sub 3-nm particles rather than in rapid measurement rate. The 3776, 3788 and the FCPC all stood out to be the faster instruments, with response times of approximately 0.5 s or less. According to the manual of TSI 3776 the instrument's 95 % response time is less than 0.8 s, with around half of this being dead time in the high flow mode. In our experiments we observed a response time of around 100 ms for the 3776, from both the spark based measurements as well as the valve based measurements. This is considerably shorter response time than that has been previously reported, and would make the instrument among faster particle counters manufactured, even faster than the TSI 3788.

One explanation for the observed speed of the TSI 3776 is the flow profile of aerosol in the instrument. The 3776 is a sheathed instrument, where sampled particles are introduced into the centerline of a saturated particle free sheath flow. This is done in order to direct the particles to pass through the region with the highest supersaturation, however this is also the location in a laminar flow profile that has the highest velocity. This means that only the fastest moving portion of the flow actually contains particles, allowing the transport of the particles to be much more homogeneous than for laminar flow instruments. It should be noted that the response time of a CPC is not determined by the speed at which the particles pass through the instrument, but rather the time difference between the fastest and slowest moving particles. This, in sheathed instruments, is made much shorter as the slowest moving portion is lacking. For unsheathed instrument, the distribution of particles in the flow field is much more heterogeneous and the response time is limited by the particles in the slower moving portions of the flow near the walls.

In light of this explanation the 3776 could well be faster than the 3788, which has a larger aerosol-to-sheath flow ratio, translating into a wider distribution of particle terminal speeds. The downside of this approach is that the gains in speed are achieved by reducing the aerosol flow, meaning poorer

counting statistics, which can act as a limiting factor in applications where the sampling speed is increased or the measured concentrations are low.

The plausibility of the unexpectedly short response time of the TSI 3776 is supported by the work of Tröstl et al. (2015), who used the 3788 and the 3776 as the detector in a scanning mobility particle sizer (SMPS), with scan times down to 3 s. In their study, the 3776 was found to do remarkably well even with the shortest of scan times. However, they also found the 3788 outperforming the 3776, which is opposite to what was found here. In their study, however, the counting statistics played a much larger role, which could partially explain the difference in their performance. The 3788 has an aerosol flow of $5 \text{ cm}^3\text{s}^{-1}$ versus $0.83 \text{ cm}^3\text{s}^{-1}$ for the 3776, translating into more than five times higher number of counts for the 3788, and therefore a considerable reduction in the uncertainty (Kangasluoma and Kontkanen 2017). For the TSI 3788, we found the response time to agree with that reported by the manufacturer. We measured it to be around 120 ms, and it is reported to be 130 ms (TSI 2013).

The ADI v-WCPC is the fastest of the unsheathed instruments tested. Its response time is around $\varepsilon = 0.7 \text{ s}$. This agrees with Hering et al. (2017), who report a value of $\varepsilon = 585 \text{ ms}$ for manual removal of an inlet filter, and 20% higher values ($\varepsilon = 700 \text{ ms}$) when testing by valve switching. (removed sentence)

5 Conclusions & Discussion

Different methodologies used to find particle counter response times were tested as a part of new CPC development work. The literature concerning CPC response time measurements was found to be light, and to have large variation both in the methodologies and definitions used. Our attempt here is to compare the different methodologies and describe the phenomena and the basic terminology required for more robust descriptions in the future. As a byproduct, we introduce a new, user friendly variation on the term response time formulated as $\varepsilon = 3 \cdot \tau$, which utilizes the widely used time constant in the representation CPCs time response. Further, we showed the potential pitfalls of the different methodologies, and give recommendation on how they should be used if these are to be used. We also present two robust methods for determining the response time, that we find to be most useful, which are the spark generation method, and the fast valve method.

The response time of a CPC is largely determined by the laminar flow profile, and the different observed response times are well explained with the different shapes, or depths, of aerosol flow profiles in the different CPCs. In sheathed CPCs the aerosol is transported in the centerline of the condenser flow in order to expose the particles to the highest possible supersaturation. The slower moving regions nearer to the walls are thus particle free air which results in a flatter aerosol particle velocity distribution than in unsheathed instruments. It should be noted that the speed of the flow is not the determining factor for a CPCs the response time, but rather the speed differences across the aerosol containing portion of the flow.

There are numerous potential sources for errors in measuring response time of fast particle counters. The simplicity of the spark method is intriguing, but the method can easily distort the results if a) the used concentrations are too high, b) one attempts to fit the concentration increase with too slow instrumentation or c) the lower detection limit coincides with the size of the measured particles. Therefore, minding dilution, turbulent flows and recording the resulting particle size distribution are recommended for future studies.

The valve method, provided that the valve used is fast enough, appears to be highly suitable for measuring response times. The method allows also the addition of an aerosol generator and size selection prior the valve for good control of aerosol properties. The method can prove problematic with pressure sensitive instruments, as there is a discontinuity in the pressure conditions, as the valve switches position. This problem is not present in the spark method.

The reporting of the response time measurement procedures should be more complete in the future, considering the number of pitfalls that can significantly distort the results. Variables such as tubing diameter, and flows or Reynolds numbers, as well as the absolute concentrations used should be reported. These crucial features help to determine if the measurements have been done correctly or if they are potentially biased.

The biggest drawback of this study was the uncertainty in the measured response times of the sheathed instrument, likely to be influenced by the pressure changes caused by the operation of the valve. These results are, however, also in agreement with the spark decay based response times, which should show no such bias, which gives us confidence in these results.

The overall recommendations of this paper for determining the response time, is either to use a fast-acting valve with switching time of few milliseconds or a spark generator. The setups presented in Figures 4 and 2, respectively, should provide a working starting point. One needs to ensure that all the flows prior to the instrument inlet are turbulent, in order to avoid smearing in the piping, and use as short tubing as possible. It is also of great importance to ensure that response time measurements are performed well below the coincidence level of the instruments and that the particle size used does not coincide with the instruments cut-off size.

Acknowledgements

This work was supported by the Maj and Tor Nessling Foundation, grants 201700367 and 201700296.

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Supplementary Information,

On the time response determination of condensation particle counters

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Table S1. List of the properties of CPC used.

| Instrument | Working fluid | Q_{inlet} (L min ⁻¹) | Q_{aerosol} (L min ⁻¹) | T_s (°C) | T_c (°C) | T_m (°C) | T_o (°C) | D_{50} (nm) | Flow mode | Reference |
|--------------|---------------|--|--|---------------|---------------|---------------|---------------|------------------|-----------|---------------------------|
| TSI 3776 | Butanol | 1.5 | 0.1 | 39 | 10 | | 39 | 2.5 | Sheated | TSI (2006) |
| TSI 3010 | Butanol | 1 | 1 | ~ 30 | ~ 13 | | 40 | 10 | Unsheated | Sem (2002) |
| TSI 3772 | Butanol | 1 | 1 | 39 | 22 | | 40 | 10 | Unsheated | TSI (2007) |
| TSI 3777 | DEG | 2.5 | 0.15 | 62 | 12 | | - | 1.4 | Sheated | TSI (2015) |
| Airmodus A20 | Butanol | 1 | 1 | 39 | 15 | | 40 | 7 | Unsheated | Airmodus (2013) |
| Airmodus A10 | DEG | 2.5 | 1 | 75-90 | 1-5 | | - | > 1.2 | Mixing | Kangasluoma et al. (2016) |
| ADI vWCPC | Water | 2.2 | 0.3 | 8 | 90 | 22 | 40 | | Sheated | Hering et al. (2017) |
| B3010 | Butanol | 1 | 1 | 55 | 10 | | > 55 | 3.2 -3.4 | Unsheated | Kangasluoma et al. (2017) |
| UHEL FCPC | Butanol | 1 | 0.3-0.7 | 39-48 | 15 | | 48 | 5 - 18 | Mixing | Here |

Table S2. Comparison of the response time fit and t_{90} , t_{50} and t_{10} times. The reported times do not include the delay time.

| | t_{10} (s) | t_{50} (s) | t_{90} (s) | $t_{95} = \varepsilon$ (s) |
|-----------------------------------|--------------|--------------|--------------|----------------------------|
| Airmodus A20, ε model | 0.038 | 0.251 | 0.834 | 1.084 |
| Airmodus A20, measured | 0.016 | 0.216 | 0.809 | 1.198 |
| Absolute difference | 0.022 | 0.035 | 0.024 | 0.114 |
| TSI 3776, ε model | 0.004 | 0.024 | 0.079 | 0.103 |
| TSI 3776, measured | 0.019 | 0.035 | 0.064 | 0.086 |
| Absolute difference | 0.016 | 0.012 | 0.015 | 0.016 |
| TSI 3772, ε model | 0.045 | 0.298 | 0.991 | 1.291 |
| TSI 3772, measured | 0.048 | 0.279 | 1.036 | 1.395 |
| Absolute difference | 0.003 | 0.019 | 0.045 | 0.104 |

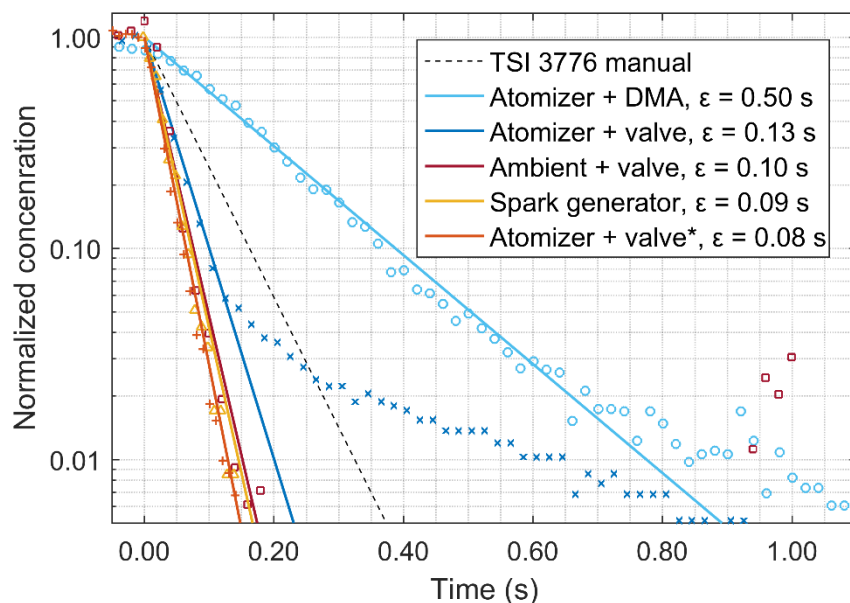


Figure S1. Comparison of different methods for determining the response time of a TSI 3776.

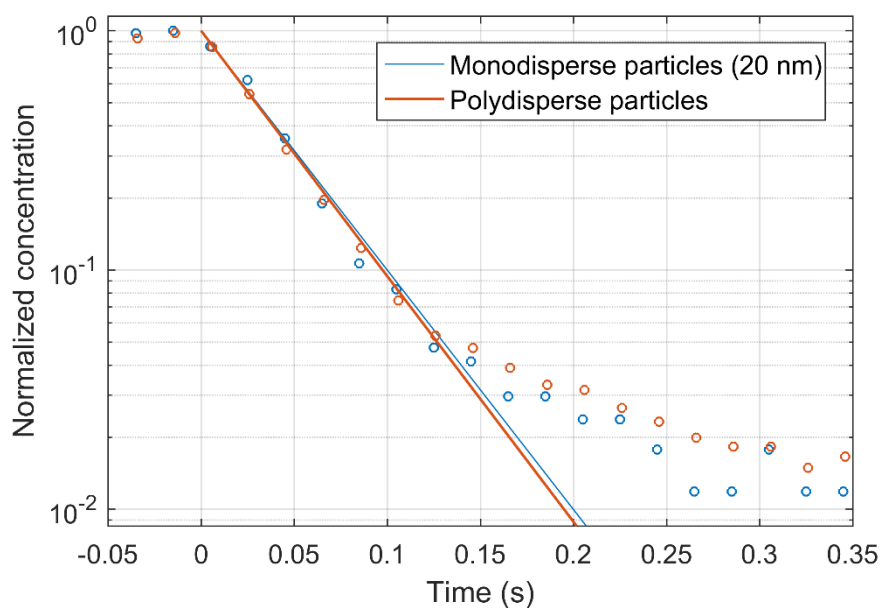


Figure S2. The response time of TSI 3776 measured using the valve method, for non-size selected particles (polydisperse) or 20 nm particles (monodisperse). It should be noted that the measurement method used is too slow for the CPC in question, but the results do show that the size of the aerosol in this range has only a negligible effect on the determined response time

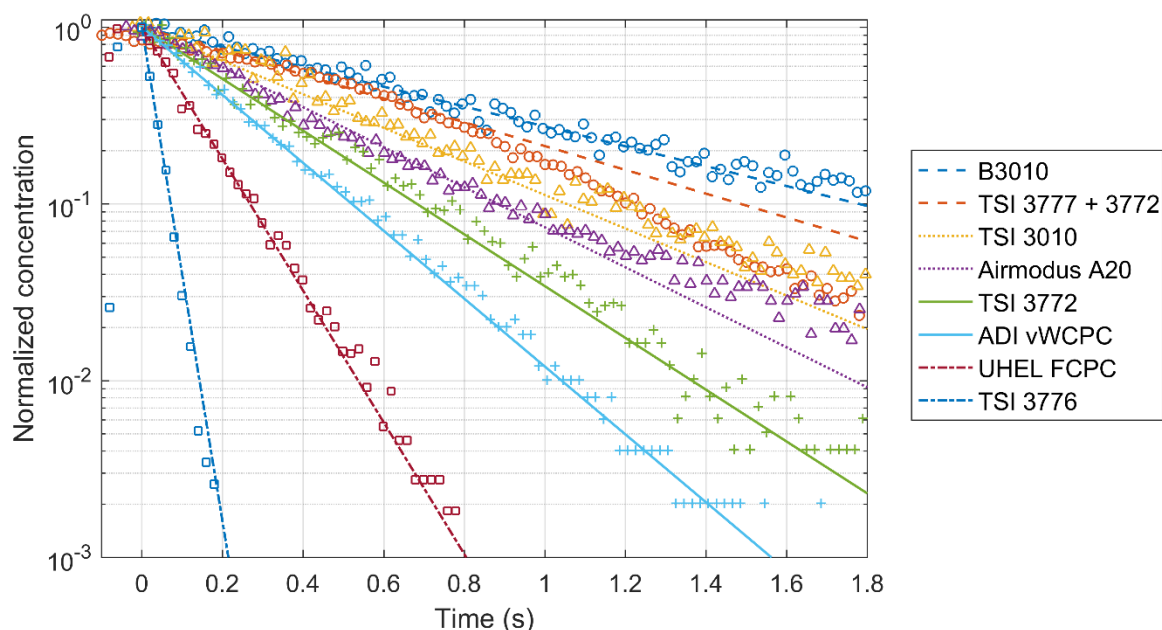


Figure S3. The response time various CPCs and the instruments presents at the CPC workshop, as determined by the spark method.

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